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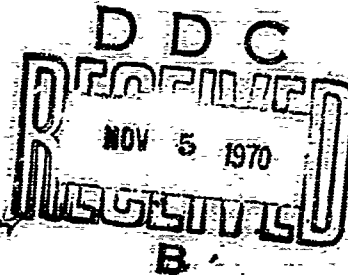
TITLE (The Vapor Pressure of Barium)

AUTHOR (P.D. Zavitsanos)

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Title Page

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<p>ABSTRACT</p> <p>The vapor pressure and the heat of vaporization of barium were measured using the Knudsen target technique. A recording microbalance was used to measure both the effusion rate and the recoil force exerted by the beam onto the target. The measured vapor pressure may be presented by</p> $\log P_{\text{atm}} = 5.145 - 9597/T$ <p>The mean heat of vaporization ΔH_{298}° as obtained by the third-law method is 43.9 ± 0.4 kcal/mole and the normal boiling point was estimated to be $2100 \pm 100^{\circ}\text{K}$.</p> <p>Mass spectrometric investigation was conducted with the time-of-flight mass spectrometer which produced a second-law heat of vaporization, $\Delta H_{298}^{\circ} = 45.1$ kcal/mole.</p>		
<p>KEY WORDS</p> <p>Vaporization, Barium, Mass Spectrometry, Microbalance</p>		

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AUTHOR P. D. Zavitsanos

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SECTION 1

INTRODUCTION

The determination of the vapor pressure of barium was first attempted by Ruff and Hartmann (Reference 1). Using the boiling point method in the temperature range 1203°K - 1410°K , these authors measured the vapor pressure and computed a second-law heat of vaporization (ΔH°_{298}) equal to 83 kcal/mole and a boiling point equal to 1419°K . The heat of vaporization (ΔH°_{298}) as calculated by the third-law method is 36.9 kcal/mole. The method was improved by Hartman and Schneider (Reference 2) who determined the vapor pressure in the temperature range 1345°K - 1408°K . The derived second-law and third-law heats, respectively, were 47 kcal/mole and 41.7 kcal/mole. The calculated boiling point is 1810°K - 1895°K . Finally, the molecular effusion target method used by Rudberg and Lempert (Reference 3) in the temperature range 798°K - 1023°K involved determination of the effusion rate by micro-titration of the evaporated deposits. These results suggest second-law heat equal to 42.27 kcal/mole and a boiling point equal to 2250°K .

In view of the observed disagreement between the various investigators with regard to the boiling point and the discrepancies between the second and third law heats, an investigation was undertaken to measure the vapor pressure of barium by the Knudsen effusion method with measurements of (a) effusion rate (by the target technique), (b) recoil force, and (c) mass spectrometric analysis.

SECTION 2 EXPERIMENTAL

2.1 MICROBALANCE MEASUREMENTS

The apparatus used in this study combines the Knudsen target technique with continuous microbalance recording of the effusion rate as well as measurement of the force exerted on the target by the impinging vapor. A detailed description and application of the apparatus has been given elsewhere (References 4 and 5).

The barium sample was obtained from the Union Carbide Co. and was KIC type contained in hollow wires of pure iron. The sample was heated by electron bombardment or radiation in a 2 x 2 cm Knudsen crucible while a well defined fraction of the effusing vapor was condensed on a collector. The collector was made from molybdenum sheet rolled to conical shape. The increase in the weight of the collector was measured with a Sartorius-Electrona microbalance and plotted by a recorder. A collimating slit of 0.475 cm radius was placed 1.2 cm above the cell orifice. The Knudsen crucible was made out of molybdenum and had an orifice 0.0057 cm^2 .

The temperature of the crucible was kept constant with an emission regulator and was measured by focussing an optical pyrometer on a black body hole drilled on the side of the crucible. The pyrometer was calibrated against an NBS lamp and all readings were adjusted for window corrections.

The rate of effusion was measured by continuously recording the weight of the target during constant temperature intervals, while the recoil force exerted (on the target) by the impinging molecules was measured by turning the effusing beam off with a shutter placed between the collimating slit and the target (Reference 4). The force is obtained from the increase in weight when the shutter (which is magnetically operated from outside the system) intercepts the beam. Figure 2-1 shows a typical weight gain curve at 1120°K , and also the apparent weight increase of the target which is related to the recoil force. The vapor pressure was then calculated by:

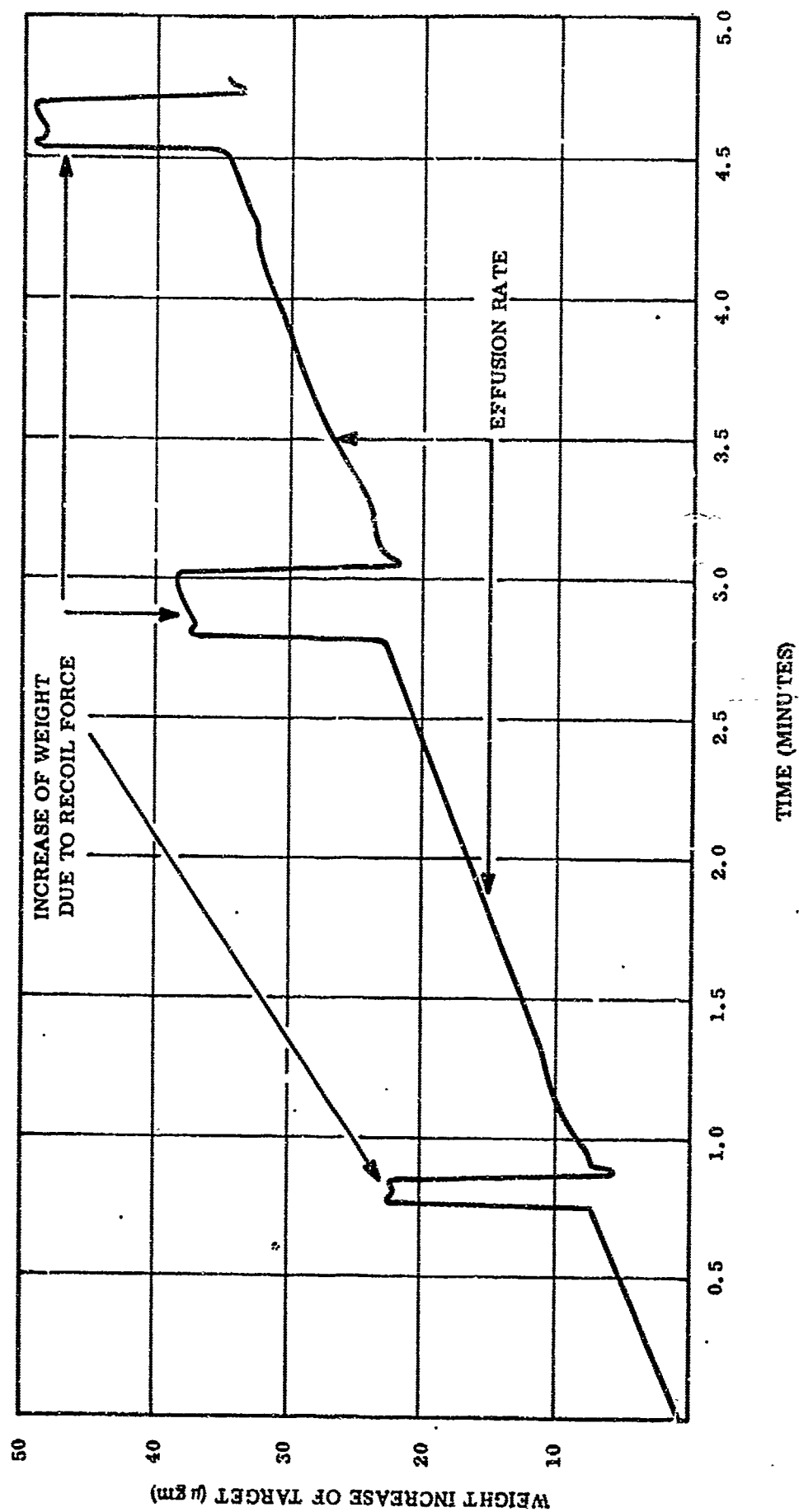


Figure 2-1. Microbalance Measurements of the Vaporization of Barium

a. The Knudsen equation:
$$P = \frac{m}{A} \left(\frac{2\pi R T}{M} \right)^{1/2} \frac{1}{\sin^2 \theta}$$

which relates the pressure inside the cell to the mass of vapor that effuses (per second) into a cone, the sides of which are at angle θ from the axis of the orifice ($\sin^2 \theta = 0.134$); m is the rate of weight gain of the target in g sec^{-1} , A is the area of the crucible orifice (0.0057 cm^2), T is the temperature, and M is the molecular weight of the effusing vapor. Based on analysis carried out in the Bendix time-of-flight mass spectrometer under the same conditions, the monatomic species was considered as the only important vapor species.

b. The recoil force method:⁶
$$P = \frac{2 F}{A (1 - \cos^3 \theta)} = \frac{2 (\Delta W) g}{A (1 - \cos^3 \theta)}$$

where $F = \Delta W \times g$ is the force exerted on the target by the beam. ΔW is the increase in the weight of the target when the beam is turned off by the shutter.

2.2 MASS SPECTROMETRIC INVESTIGATION OF VAPOR

The vapor effusing from a Knudsen crucible containing Ba was examined with the Bendix time-of-flight mass spectrometer using a 20-volt electron beam. The tantalum crucible containing barium was mounted so that the orifice was in line with the entrance slit of the ion source (after going through a series of shields and the slit of the isolation valve). The furnace was pumped differentially by a 4-inch Hg diffusion pump and a mechanical pump which provided a background pressure of less than 10^{-6} torr. The crucible was heated by radiation from a tungsten filament (surrounding it). The temperature was measured by sighting into the crucible orifice with a calibrated optical pyrometer. Inspection of the barium isotopes was made over the temperature range $1063^\circ\text{K} - 1253^\circ\text{K}$.

SECTION 3

RESULTS AND DISCUSSION

The results of the vaporization studies on barium are summarized in Tables 3-1, 3-2 and 3-3. Rates of effusion were obtained by continuously weighing the target (Table 3-1) and obtaining slopes $\frac{\Delta W}{\Delta t}$ corresponding to weight changes (ΔW) of several hundred micrograms and times (Δt) several minutes. Combination of the vapor pressure data with corresponding free energy functions from Stull and Sinke (Reference 7) produced values for the heat of vaporization at 293⁰ K (based on the third-law method) equal to 44.01 ± 0.31 kcal. mole⁻¹, and 43.83 ± 0.54 kcal. mole⁻¹ from the effusion rate data and from the recoil force measurements, respectively. The agreement between the two methods is quite good. If one uses the average value of $\Delta H_{298}^0 = 43.9 \pm 0.4$ and the free energy functions, the vapor pressure is represented by $\log P_{\text{atm}} = -\frac{9597}{T} + 5.145$ and a boiling point of 2100 ± 100^0 K is calculated.

A typical ionization efficiency curve for barium as obtained by mass spectrometric analysis is shown in Figure 3-1. The appearance potential of Ba⁺ is about 5 eV and is indeed close to the reported ionization potential of Ba (i.e., 5.19 eV). The structure observed at higher electron energies (i.e., 8 - 10 eV) is similar to that reported for calcium (Reference 8) and could possibly be due to neutral or ion excited states.

The mass spectrometric measurements made at 20 eV are shown in Table 3-3 and Figure 3-2 in terms of intensity for the barium ions (I_{Ba^+}) vs. temperature. From the slope of a $\log (I_{\text{Ba}^+} \times T)$ vs. $1/T$ plot, a second law heat $\Delta H_{298}^0 = 45.1$ kcal/mole is obtained. This value is in rather good agreement with the third-law values of 44 and 43.8.

These results are to be compared with all previous work (Reference 5, 6, 7, and 8) shown in Figure 3-3 and Table 3-4.

Table 3-1. Vapor Pressure Data on Barium Metal -
from Effusion Rate Measurements

$T^{\circ} \text{K}$	$10^4/T$	Rate ($\mu\text{g min}^{-1}$)	$-\log P$ (atm.)	ΔH°_{298} (kcal. mole $^{-1}$)
1120	8.93	255	3.499	44.17
1164	8.59	600	3.069	43.87
1209	8.27	1428	2.685	43.08
1119	8.94	260	3.44	44.06
1144	8.74	322	3.342	44.43
1144	8.74	346	3.311	44.27
1144	8.74	342	3.316	44.27
1138	8.78	274	3.65	44.29

$$\Delta H^{\circ}_{298} \text{ (ave.)} = 44.01 \pm 0.31$$

Table 3-2. Vapor Pressure Data on Barium Metal
from Recoil Force Measurements

$T^{\circ}\text{K}$	ΔW (μg)	$-\log P$ (atm.)	ΔH°_{298} (Kcal. mole ⁻¹)
1134	250	3.486	44.19
1215	850	2.828	44.45
1156	200	3.456	45.55
1162	300	3.280	44.70
1113	300	3.280	43.03
1122	380	3.177	42.82
1128	400	3.155	42.92
1125	460	3.094	42.51
1125	333	3.235	43.24
1139	300	3.280	43.94
1164	460	3.094	43.78
1147	350	3.566	43.95
1140	350	3.213	43.63
1138	300	3.280	43.91
1102	200	3.456	43.54
1102	160	3.806	45.29
1166	650	3.036	43.57
1126	240	3.376	43.98

$$\Delta H^{\circ}_{298} = 43.83 \pm 0.54$$

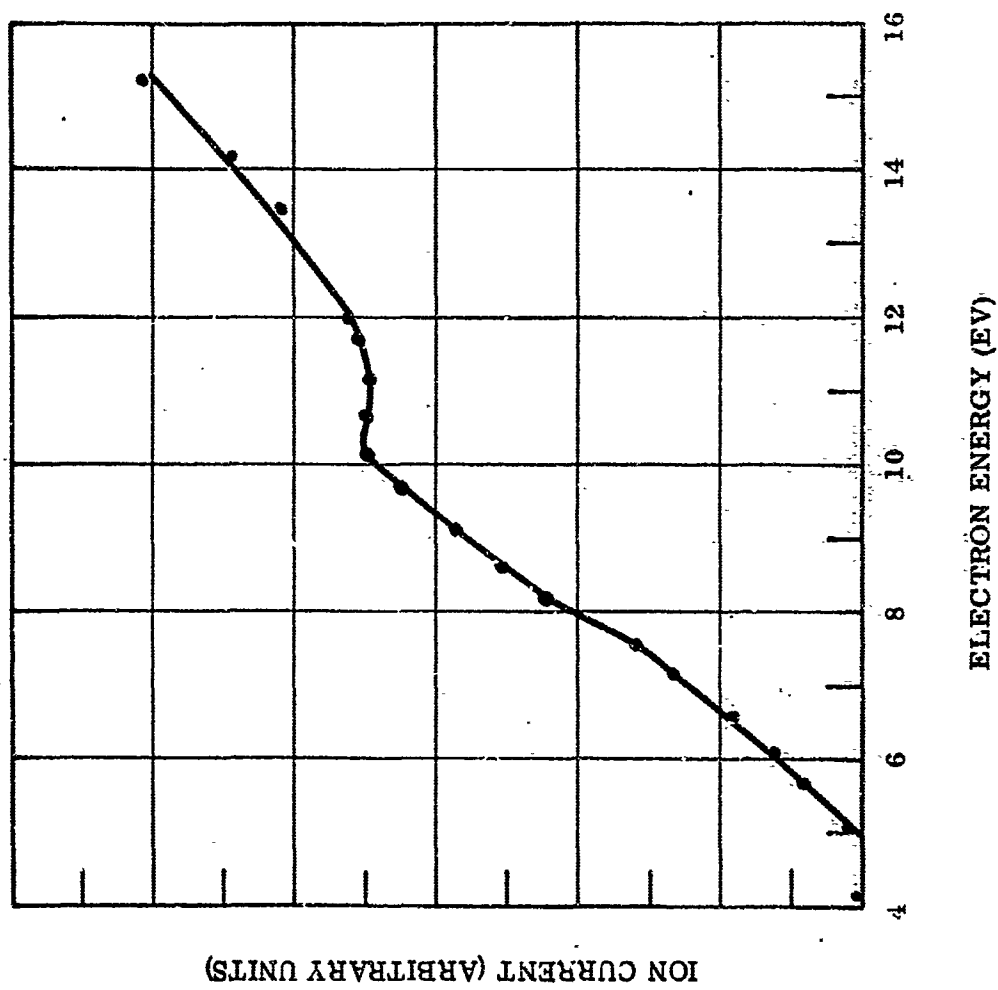


Figure 3-1. Ionization Efficiency Curve for Barium

Table 3-3. Mass Spectrometric Investigation of Barium Vapor

$T^{\circ}\text{K}$	$10^4/T$	$I_{\text{Ba}}^+ \times T$	$\log (I_{\text{Ba}}^+ \times T)$
1253	7.98	33.46	1.52
1253	7.98	37.13	1.58
1228	8.14	23.24	1.36
1228	8.14	30.70	1.49
1228	8.14	30.70	1.49
1193	8.38	14.91	1.17
1193	8.38	14.91	1.17
1198	8.35	14.61	1.16
1158	8.63	5.37	0.98
1158	8.63	4.94	0.95
1158	8.63	5.15	0.97
1158	8.63	4.29	0.89
1063	9.41	2.13	0.33
1063	9.41	1.86	0.27
1063	9.41	1.59	0.20

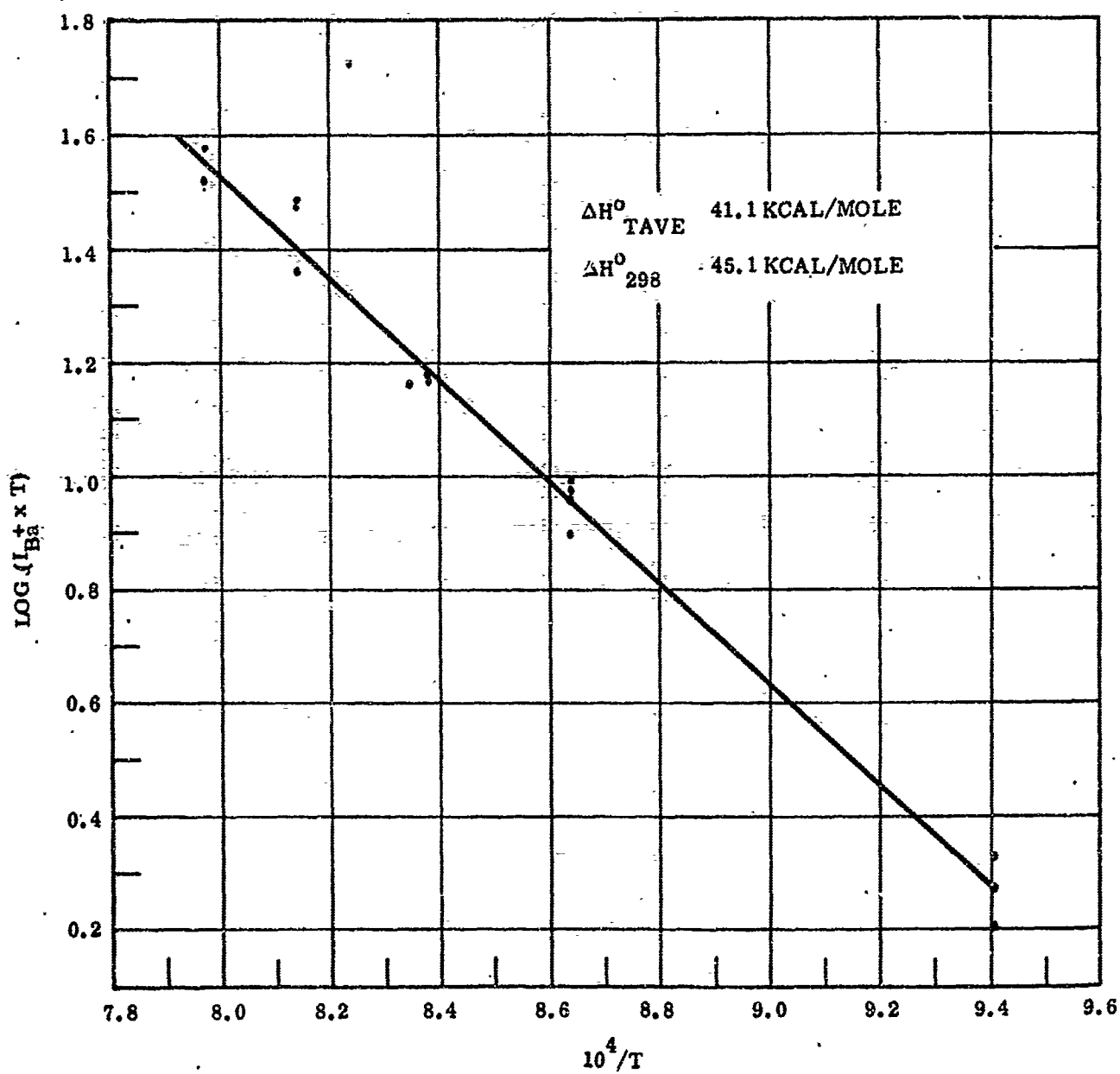


Figure 3-2. Clausius-Clapeyron Plot for Ba(g) above Ba(l)

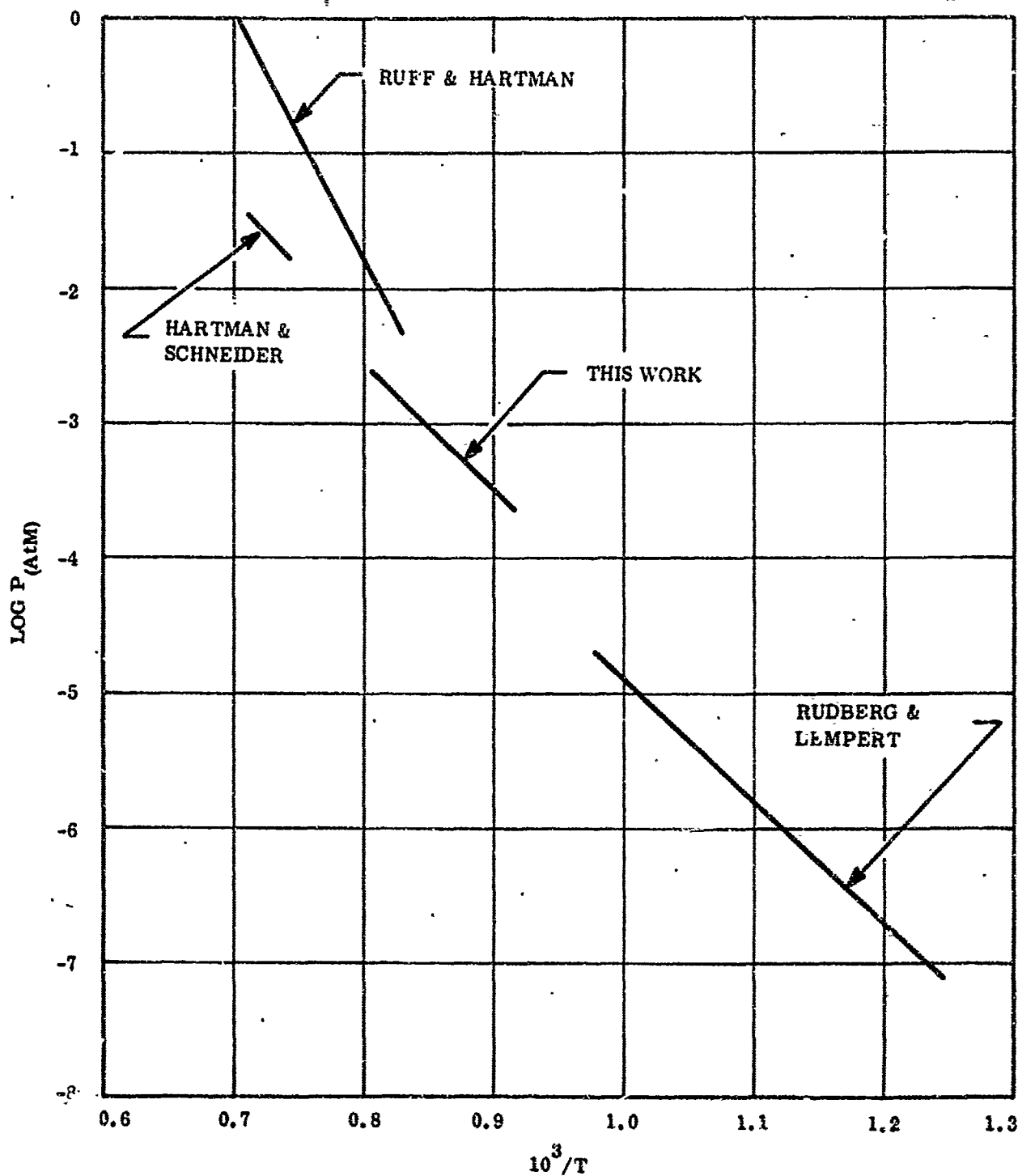


Figure 3-3. Vapor Pressure of Barium

Table 3-4. Results

<u>Method</u>	<u>ΔH°_{298}</u>	<u>Boiling Point ($^{\circ}\text{K}$)</u>	<u>Reference</u>
Boiling Point			1
(a) 2nd Law	83.1	1419	
(b) 3rd Law	36.9		
Boiling Point			2
(a) 2nd Law	47.0		
(b) 3rd Law	41.7	1810	
Effusion (Target)			3
(a) 2nd Law	42.47	2250	
Effusion (Target)			this work
(a) Effusion Rate 3rd Law	44.0 ± 0.3		
(b) Recoil Force 3rd Law	43.8 ± 0.5	2100 ± 100	
(c) Mass Spectrometry 2nd Law	45.1 ± 0.6		

SECTION 4

CONCLUSIONS

In view of the agreement between the three different techniques used in this investigation and the reproducible values of the heat of vaporization obtained by the second and third law methods it is concluded that a more accurate value for the heat (ΔH_{298}^0) is 44.3 ± 0.5 kcal/mole. Furthermore recent optical measurements (Reference 9) support a heat value higher than 42.47 kcal*.

* This value has been adapted by Hultgren in his tabulation of Thermo. Prop. of Metals and Alloys, 1968.

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